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Naval Surface Warfare Center
Bethesda, MD 20084–5000

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Ship Materials Engineering Department
Research and Development Report

Effect of the Addition of Al_2O_3 and Ag_2O on the Morphology and Superconductivity of $YBa_2Cu_3O_{6+X}$ Ceramic Materials

by
A. Srinivasa Rao

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ABSTRACT

In order to produce $YBa_2Cu_3O_{6+x}$ ceramic material with fine particle size and good superconducting properties, both Al_2O_3 and Ag_2O were added to $YBa_2Cu_3O_{6+x}$ during sintering. The results suggest that the addition of both Al_2O_3 and Ag_2O does not decrease the average particle size of $YBa_2Cu_3O_{6+x}$; however, the superconducting properties degrade with an increase in the Al_2O_3 concentration. In composites containing high additive concentration, fine structure resembling that of fine pits is discernible on $YBa_2Cu_3O_{6+x}$ particles.

ADMINISTRATIVE INFORMATION

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INTRODUCTION

The advancement of superconducting ceramic materials with zero resistance above liquid nitrogen temperature [1,2], has prompted a race for fabricating these brittle ceramics into useful components. Although the fabrication of superconducting ceramic thin films has been explored using various techniques, such as ion beam deposition, vapor phase deposition etc. [3-6], no significant advancement in the processing of bulk ceramics has been achieved to date. This project was undertaken in order to study the feasibility of extruding bulk superconducting

ceramic into wires or tapes using the superplastic deformation technology.

The important requirement that has to be met for maximum superplastic deformation is to maintain a small grain size (less than 5×10^{-7} m) [7,8]. In this study, the main focus has been to define and determine the processing parameters for producing bulk superconducting ceramic preform with fine grain size and high T_c. Some of the experimental results relating the effect of the addition of both Al_2O_3 and Ag_2O, on the crystal structure, morphology and superconducting properties of $YBa_2Cu_3O_{6+x}$ are presented here.

EXPERIMENTAL PROCEDURE

The basic $YBa_2Cu_3O_{6+x}$ superconducting ceramic powder was prepared by solid state reaction of yttrium oxide, copper (II) oxide and barium carbonate. The precursor mixture was ball milled with distilled water for 2 hours using zirconia balls. The suspension was dried for 24 hours at 110°C. The dry powder was calcined at 940°C for 6 hours and cooled slowly (at the rate of 2°C/min) to room temperature. Later the superconducting ceramic powder was ground using a mortar and pestle in order to ensure homogeneous composition.

Two additives, alumina and silver oxide were chosen for this investigation. It is because alumina was reported to exhibit superplastic deformation above 1000°C [7-8], which is close to the range of temperatures at which these superconducting ceramic

materials might be deformed. In addition, we have also reported earlier [9], that the addition of alumina to the superconducting $YBa_2Cu_3O_{6+x}$ prior to the calcination (at 920°C), inhibits the grain growth of $YBa_2Cu_3O_{6+x}$ during sintering process. The additive silver oxide was selected because, Ag_2O decomposes on heating to sintering temperatures, thus silver possibly may help the onset of superplasticity. Secondly, it was also observed that the free oxygen liberated during the decomposition process, was frequently taken up by the oxygen deficient $YBa_2Cu_3O_{6+x}$ structure. The flow diagram of the processing of $YBa_2Cu_3O_{6+x}$/ additive composites is shown in Figure 1. Pre - determined amounts (in the range 0 - 30 wt %) of both alumina and silver oxide (average size 10 X 10^{-6} m) were added to the $YBa_2Cu_3O_{6+x}$ powder. The mixture was ball milled and dried using the above procedure. The dry homogeneous mixture of the additive and the superconducting powder was dry pressed into 1 cm discs. The green disc samples were sintered at 920°C in air for 2 hours, cooled slowly in air to 600°C (at the rate of 1°C/min). The samples were annealed at 600°C for 6 hours and cooled to room temperature (at the rate of 2°C/min).

The particle size and surface area of the powders was determined by sedigraph and single point BET apparatus respectively. The additive distribution, the particle morphology of sintered samples was analyzed using (back scattered and secondary) scanning electron microscopy. The structural characteristics and the electrical properties of the composites was determined using x - ray diffraction and four

probe resistivity methods respectively.

RESULTS

Pure $YBa_2Cu_3O_{6+x}$

Figure 2 shows a typical elongated rod like morphology of $YBa_2Cu_3O_{6+x}$ particles in sintered bulk ceramic, with a major axis length of approximately $40 \pm 20 \times 10^{-6}$m and (mostly) orthorhombic in crystal structure. The average particle size, powder density and surface area of the as-synthesized powder was approximately 10×10^{-6}m, 6.0 gm/cm^3 and 0.22 m^2/gm respectively. The above results (based on the particle size consideration alone) indicates that while superconducting $YBa_2Cu_3O_{6+x}$ ceramic material in pure state is (too large to exhibit any significant superplasticity) not suitable for superplastic deformation, the particle size in as-synthesized powder form is suitable for the study of the effect of additives on grain size control during sintering.

Alumina and Silver Oxide Additions

Earlier, it was shown [9] that additive alumina tends to reduce the particle size of $YBa_2Cu_3O_{6+x}$ (the maximum reduction being 400 % due to the addition of about 10 wt. % alumina) and silver oxide shows no effect on the reduction of the superconducting ceramic material particle size. In spite of the success with the reduction of the average particle size, the results indicate that the superconducting properties of alumina composites deteriorated. Figure 3 shows the electrical resistivity versus temperature profiles of pure $YBa_2Cu_3O_{6+x}$, 5

wt.% Al_2O_3 and 5 wt.% Ag_2O composites. From the above results it can be postulated that a combination of additives may improve both the electrical properties and the process of particle size reduction during sintering.

Figure 4 shows typical morphology of 2 wt.% Al_2O_3/5, 10 and 15 wt.% $Ag_2O/YBa_2Cu_3O_{6+x}$ composites. The results suggest that the addition of both Al_2O_3 and Ag_2O has no significant effect on the particle size of $YBa_2Cu_3O_{6+x}$. In order to obtain a semi - quantitative estimate of the particle size as a function of both alumina and silver oxide concentration, number of micrographs representing the morphology of all sintered composites were obtained from random areas. Figure 5 shows the average particle size of $YBa_2Cu_3O_{6+x}$ versus additives Ag_2O and Al_2O_3 concentration. The results suggest that the particle size reduction depends upon the concentration of Ag_2O. At higher concentrations ($\geq$ 10 wt.%), the addition of Al_2O_3 has very little effect on the particle size.

The results on the superconducting transition temperature of all the samples is shown in Figure 6. The results suggest that the addition of silver oxide to the alumina/$YBa_2Cu_3O_{6+x}$ system improves the superconducting transition temperature.

DISCUSSION

Optimization of processing methodology often produces sintered ceramic materials of required microstructure, particle size and mechanical and electrical properties. The results of the present investigation suggests that the processing method

used here, for the composite preparation has not produced the anticipated fine microstructure (average grain size of 500 nm). However, it has shown that the superconducting properties of $Al_2O_3/YBa_2Cu_3O_{6+x}$ composites can be improved with the addition of Ag_2O. In addition, the important observation that has to be acknowledged is the identification of fine microstructure with in the grains of the superconducting $YBa_2Cu_3O_{6+x}$.

Previous investigations [9] have indicated that the mechanism of particle size reduction due to the addition of Al_2O_3 is very complex. However, based on the microstructural observations in $YBa_2Cu_3O_{6+x}$, it can be postulated that the additive Al_2O_3 probably attacks and erodes the surface of $YBa_2Cu_3O_{6+x}$. The question that was not answered was whether the erosion process is chemical or purely a physical phenomena. From the microstructural results of the present investigation, it may be possible to explain the mechanism of the particle size reduction process. The morphology of the particles of $Al_2O_3/Ag_2O/YBa_2Cu_3O_{6+x}$ shown in Figure 4 does not show any abnormal anomaly. However, a careful examination of the microstructure of composites containing higher concentrations of both Al_2O_3 and Ag_2O suggests that fine platelet like pits develop on the surface of $YBa_2Cu_3O_{6+x}$. No such features are discernible either on Al_2O_3 or Ag_2O particles. Figure 7 shows a typical morphology of sintered composite containing 5 wt % Al_2O_3 and 5 wt % Ag_2O.

If it is assumed that these fine pits were produced during

the initial stages of the erosion of $YBa_2Cu_3O_{6+x}$ by Al_2O_3, it is possible to suggest a simple mechanism for the particle size reduction process as follows : the additive Al_2O_3 chemically attacks the lattice of $YBa_2Cu_3O_{6+x}$ and in doing so it results in the depletion of oxygen from the lattice. Chemical destabilization due to the removal of oxygen, $YBa_2Cu_3O_{6+x}$ transforms into non superconducting Y_2BaCuO_5. A continued break in the lattice bonds and transformation of the chemical structure of $YBa_2Cu_3O_{6+x}$ produces fine particle size and also the deterioration of the superconducting properties of the composite. Although both of the final results were observed experimentally [9], no unequivocal direct evidence supporting the above mechanism has been achieved.

However, it can be suggested that if the oxygen depletion from $YBa_2Cu_3O_{6+x}$ degrades the superconductivity, the above process can be controlled by supplying oxygen to Al_2O_3 during sintering. Such process, then will not only improve the superconductivity, but may also inhibit the particle size reduction process. The results of the present investigation supports the above hypothesis that when oxygen (which is the decomposition product of Ag_2O) is supplied to Al_2O_3 during sintering, it inhibits both the particle size reduction and degradation of superconducting properties of the composite. In order to understand the detailed mechanism of this process, high resolution transmission electron microscope analysis of these fine features is being carried out and the results of that analysis will be reported at a later date.

CONCLUSION

From the present investigation, the following conclusions can be derived :

1. Addition of both Al_2O_3 and Ag_2O to $YBa_2Cu_3O_{6+x}$ during sintering does not affect the particle size of $YBa_2Cu_3O_{6+x}$ significantly.

2. Addition of Ag_2O to $Al_2O_3/YBa_2Cu_3O_{6+x}$ composites, improves the superconducting properties of the composite.

3. Composites containing higher concentrations of additives (Al_2O_3 and Ag_2O) show fine pit like features on $YBa_2Cu_3O_{6+x}$ particles.

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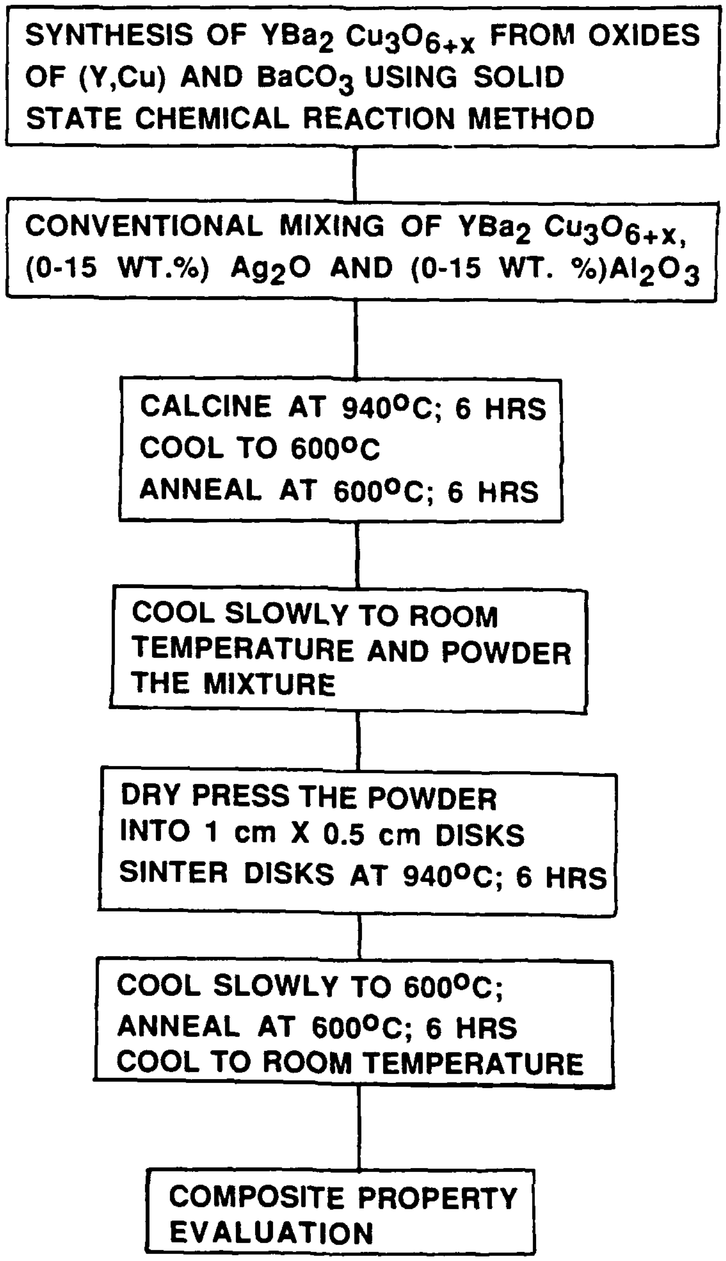

Figure 1. Flow Diagram of the Processing of $Al_2O_3/Ag_2O/YBa_2Cu_3O_{6+x}$ Composites.

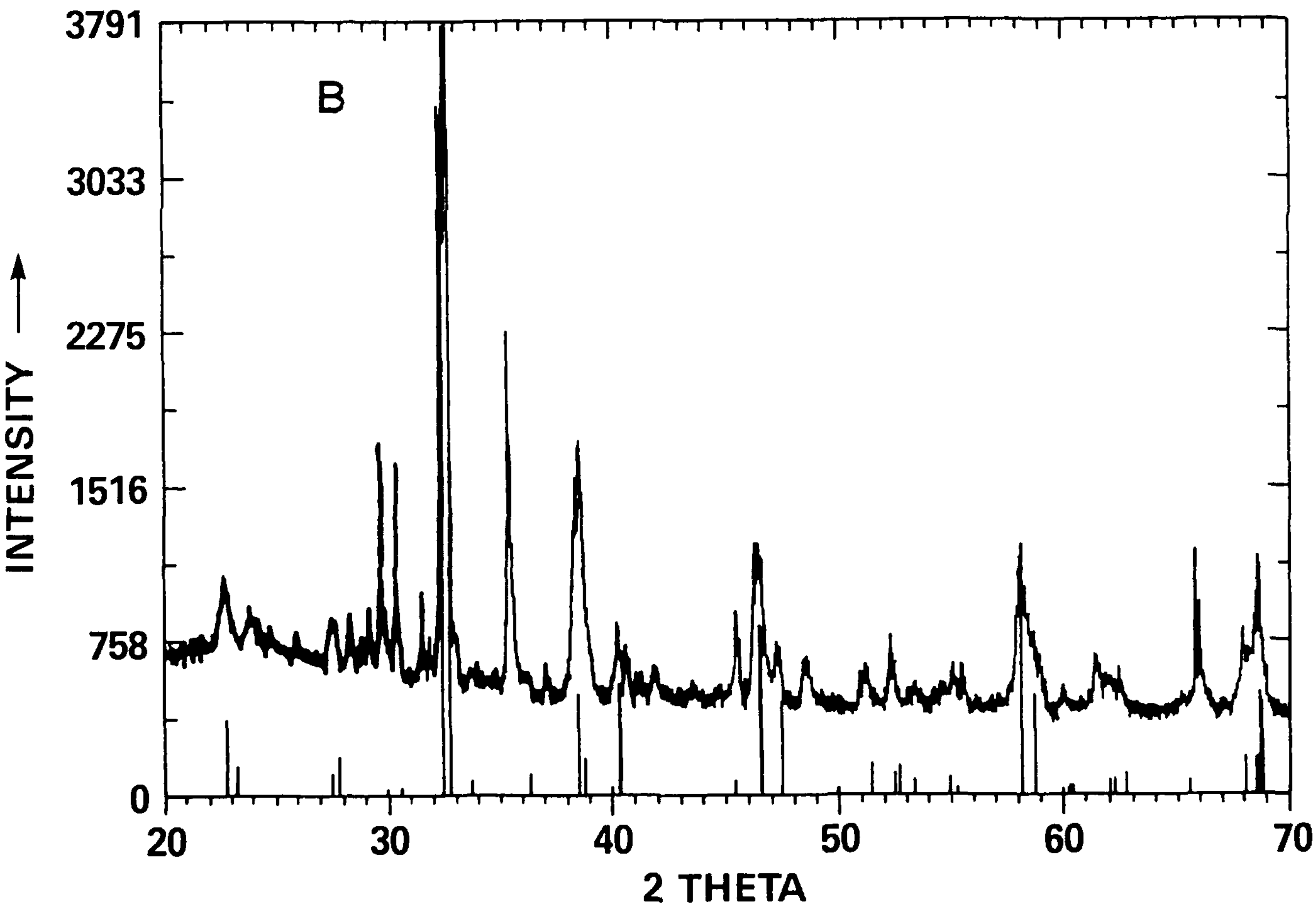

Figure 2. Typical (A) Morphology and (B) Structure of Sintered $YBa_2Cu_3O_{6+x}$ Superconducting Ceramic.

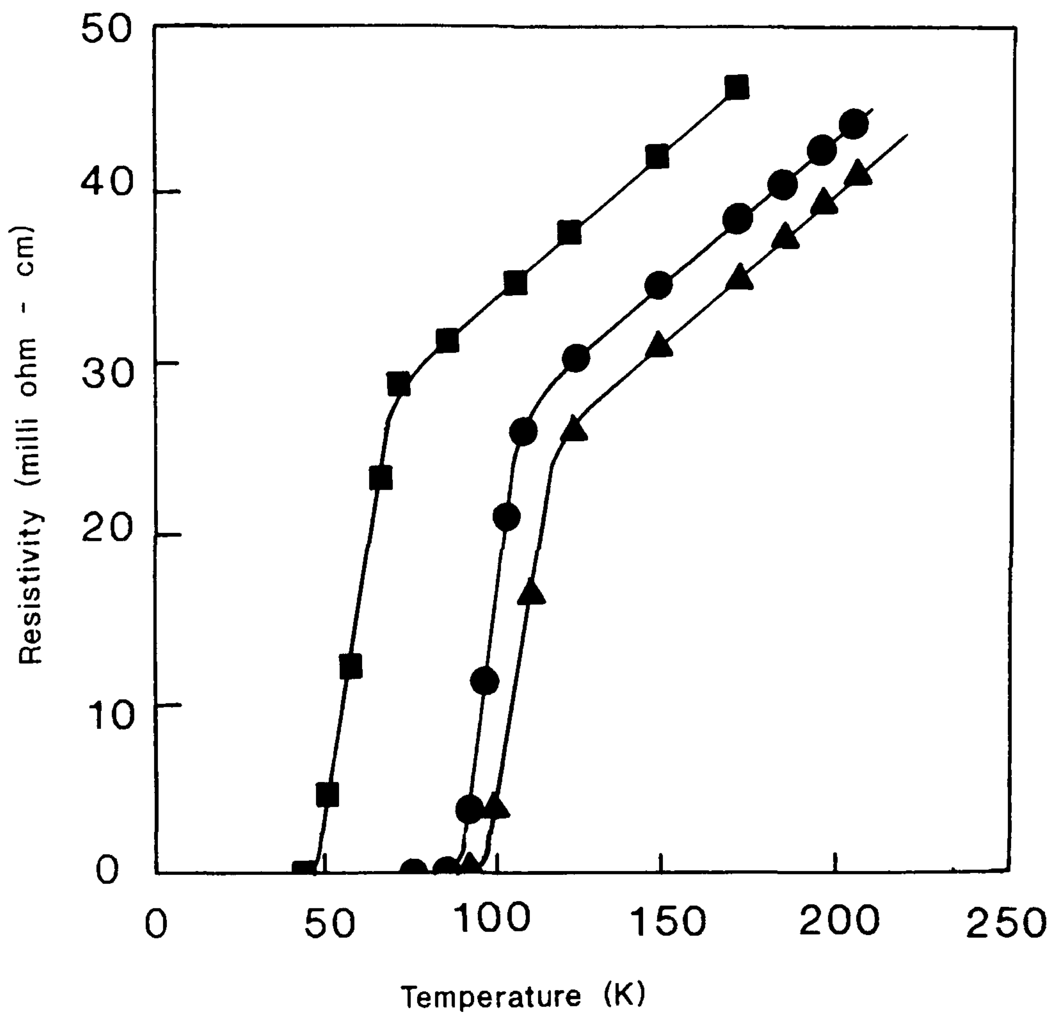

Figure 3. Electrical Resistivity versus Temperature Profiles of Sintered (●) Pure $YBa_2Cu_3O_{6+x}$, (■) 5 wt.% Al_2O_3/$YBa_2Cu_3O_{6+x}$ and (▲) 5 wt.% Ag_2O/$YBa_2Cu_3O_{6+x}$ Composites.

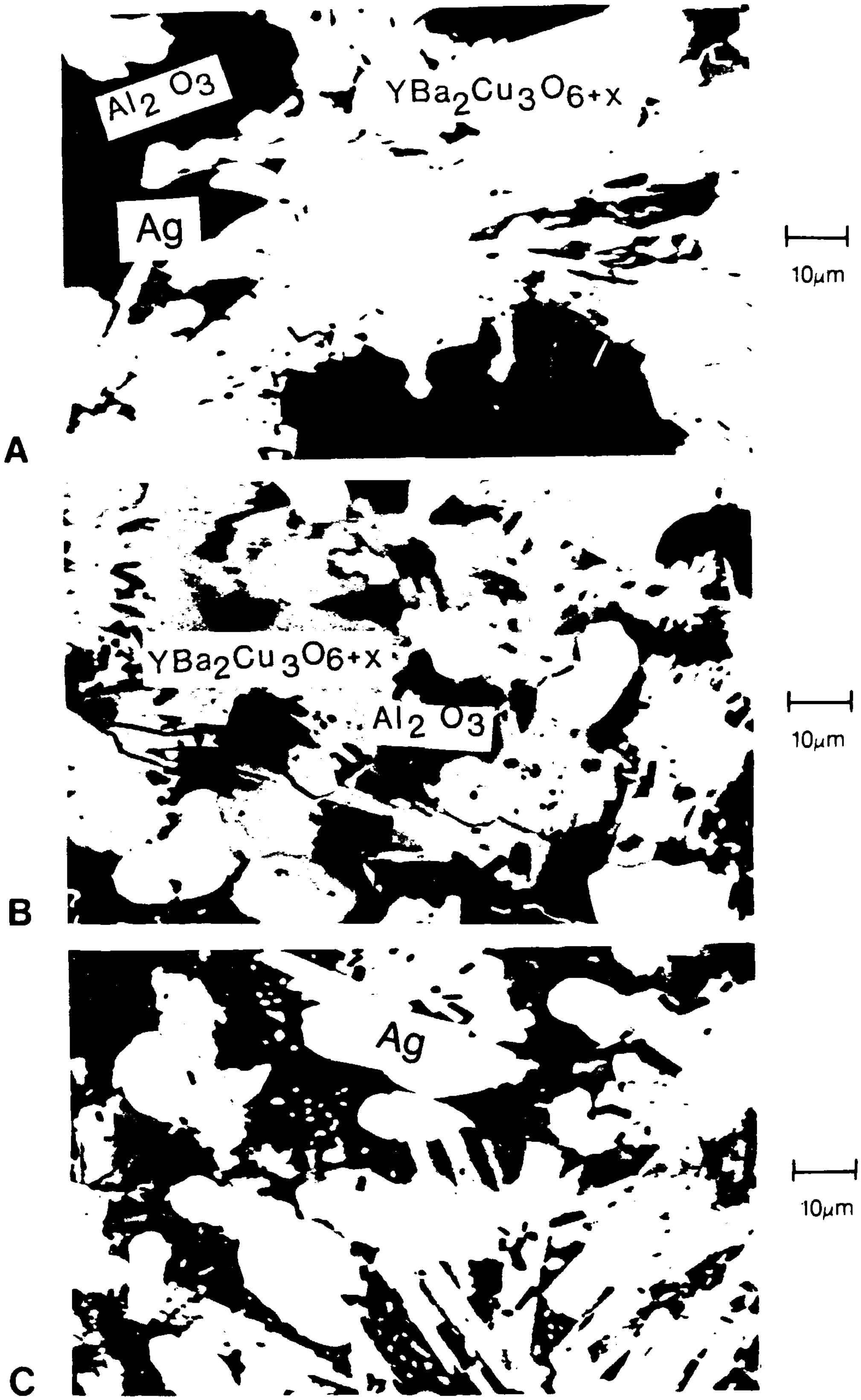

Figure 4. Scanning Electron Micrographs of the Morphology of $Al_2O_3/Ag_2O/YBa_2Cu_3O_{6+x}$ Composites. Concentration of Additives : Al_2O_3 2 wt.% and Ag_2O (A) 5, (B) 10 and (C) 15 wt.%.

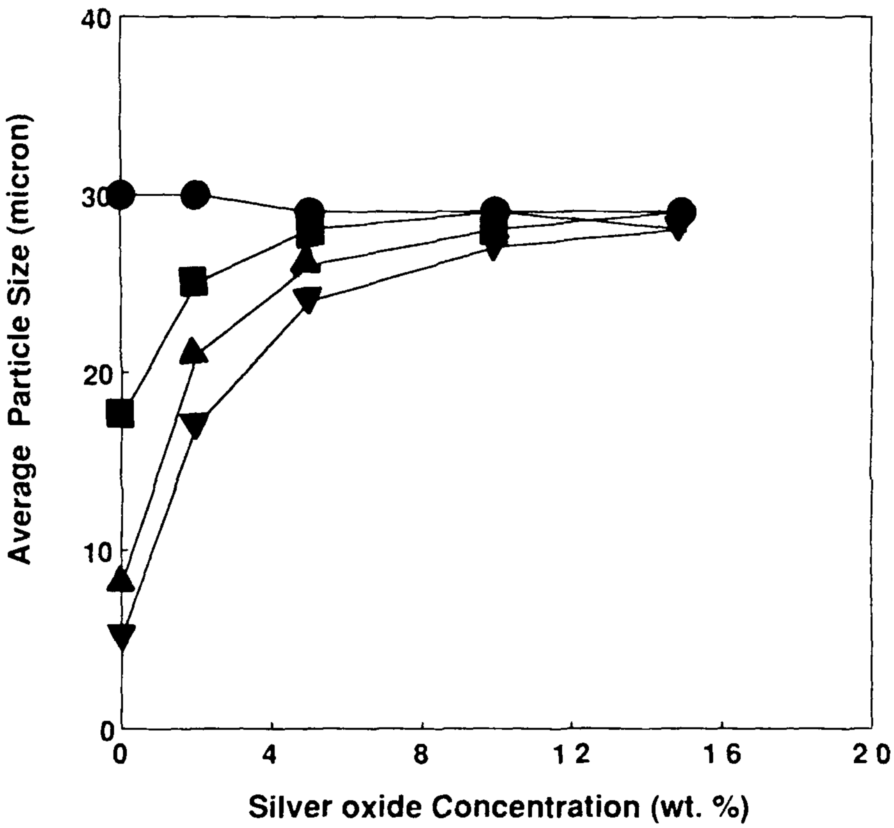

Figure 5. Average Particle Size of $YBa_2Cu_3O_{6+x}$ versus Ag_2O Concentration Profiles of $Al_2O_3/Ag_2O/YBa_2Cu_3O_{6+x}$ Composites. Al_2O_3 Concentration (●) 2, (■) 5, (▲) 10 and (▼) 15 wt.%.

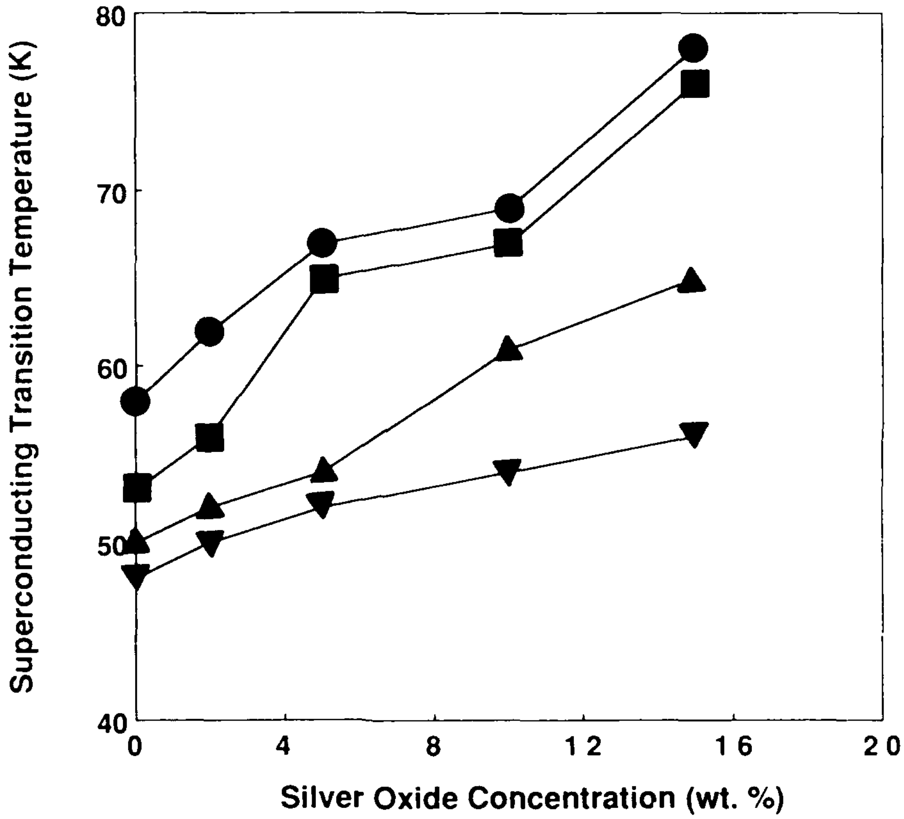

Figure 6. Superconducting Transition Temperature versus Ag_2O Concentration Profiles of $Al_2O_3/Ag_2O/YBa_2Cu_3O_{6+x}$ Composites. Al_2O_3 Concentration (●) 2, (■) 5, (▲) 10 and (▼) 15 wt.%.

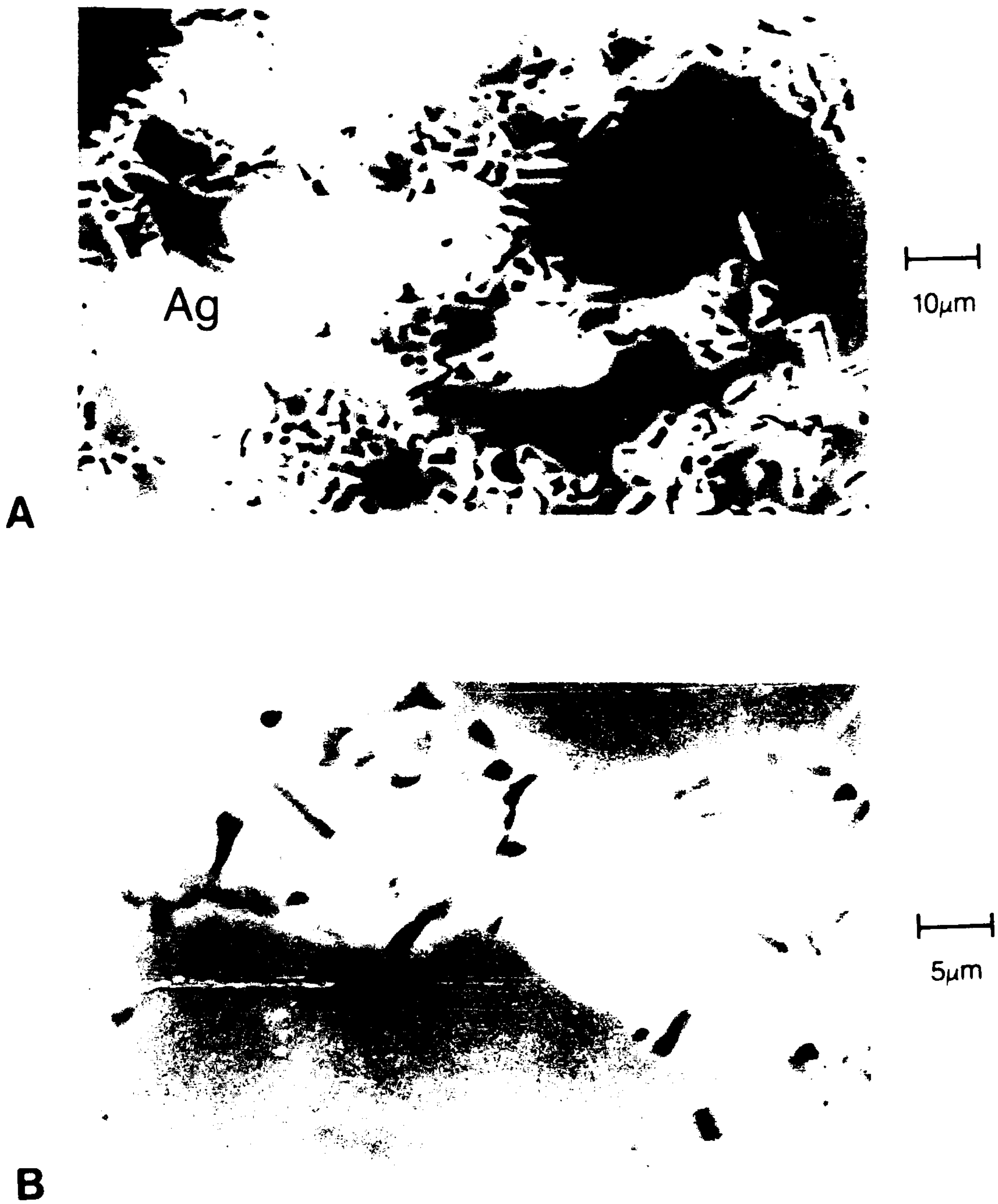

Figure 7. Scanning Electron Micrographs of the Morphology of Sintered 5 wt.% Al_2O_3/ 5 wt.% Ag_2O/ $YBa_2Cu_3O_{6+x}$ Composite.

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13. ABSTRACT (Maximum 200 words)

In order to produce $YBa_2Cu_3O_{6+X}$ ceramic material with find particle size and good superconducting properties, both Al_2O_3 and Ag_2O were added to $YBa_2Cu_3O_{6+X}$ during sintering. The results suggest that the addition of both Al_2O_3 and Ag_2O does not decrease the average particle size of $YBa_2Cu_3O_{6+X}$; however, the superconducting properties degrade with an increase in the Al_2O_3 concentration. In composites containing high additive concentration, fine structure resembling that of fine pits are discernible on $YBa_2Cu_3O_{6+X}$ particles.

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